

Reaction Engineering International

Advanced Computer Simulations Of Military Incinerators

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Outline

- ➔ Technical objectives of SBIR project
- ➔ Chemical kinetic mechanism
development for agent destruction
- ➔ Equipment model development
- ➔ Applications of models

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SBIR Phase II Technical Tasks

➔ Develop Chemistry Models for CWA

- ◆ effort guided by Advisory Panel
- ◆ use computational chemistry methods
- ◆ simulants & agents
- ◆ detailed chemical kinetic mechanisms
 - » complete description of CWA decomposition
 - » include PICs, NOx
 - » use relevant, publicly available data

➔ Develop Furnace / Equipment Models

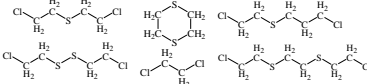
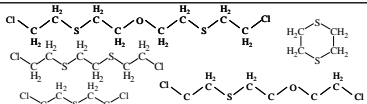
- ◆ Incinerators: furnaces + afterburners
- ◆ Pollution Abatement System (PAS)
- ◆ benchmark with available data

➔ Develop Incinerator Simulator Tool Software



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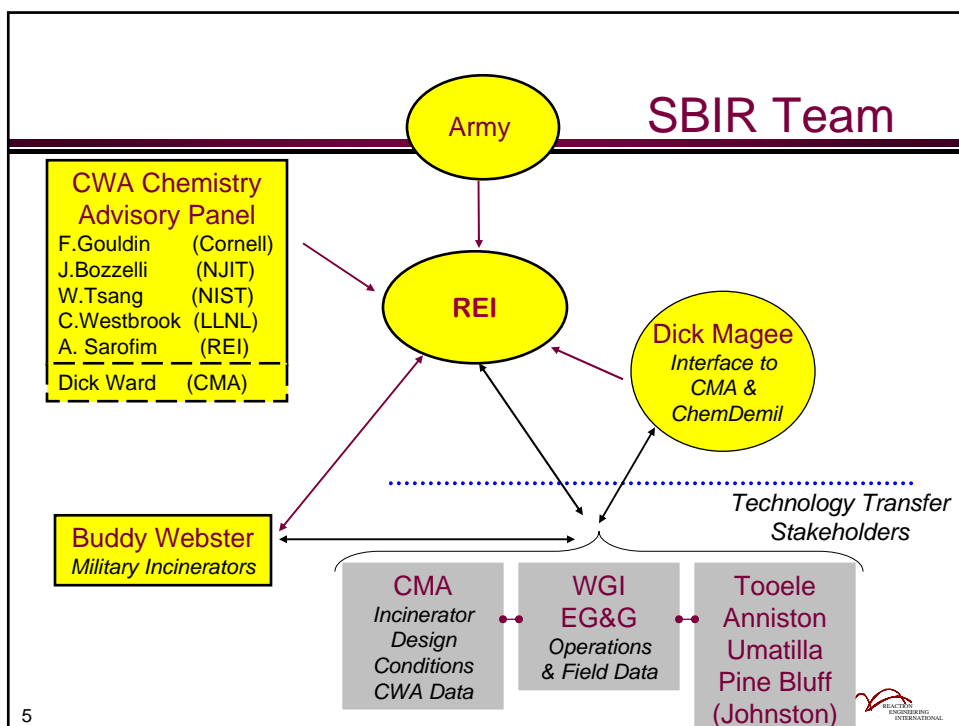
Chemistry Models for CWA's

Agent	Structure	Mechanism
GB	$ \begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{O}-\text{P}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{F} \end{array} $	LLNL w/ Bozzelli-REI GB rate + P & F
VX	$ \begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5-\text{O}-\text{P}-\text{S}-\text{C}_2\text{H}_4-\text{N} \begin{array}{l} \nearrow i\text{-C}_3\text{H}_7 \\ \searrow i\text{-C}_3\text{H}_7 \end{array} \\ \\ \text{CH}_3 \end{array} $	Bozzelli-REI
HD	$ \begin{array}{c} \text{H}_2 \quad \text{H}_2 \\ \quad \\ \text{Cl}-\text{C}=\text{C}-\text{S}-\text{C}=\text{C}-\text{Cl} \\ \quad \\ \text{H}_2 \quad \text{H}_2 \end{array} $	Bozzelli-REI
H		Bozzelli-REI
HT		Bozzelli-REI

- Reliable test data not available
- Developed using computational chemistry methods
 - 100+ species
 - 500-1200 reactions
- Benchmarked with known rate constants for comparable molecules
- Reviewed by expert Advisory Panel



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Chemical Kinetic Mechanism for H/HD/HT

- No test data available – rates from computational chemistry
- Kinetics for thickeners and impurities included
- HD detailed mechanism:
 - ◆ 109 species, 477 reactions
 - ◆ Couples to
 - » Leeds sulfur mechanism
 - » Cl chemistry of Procaccini, Ho, Bozzelli, et al
- H modeled by 6-specie blend
 - ◆ 5 species for impurities
 - ◆ Add-on to HD mechanism
 - ◆ 143 species, 548 reactions
- HT modeled by 5-specie blend
 - ◆ 4 species for impurities
 - ◆ Add-on to H/HD mechanism
 - ◆ 165 total species, 657 total reactions
- Improvements to S-H-O chemistry

Dominant destruction pathway:
HCl elimination from HD

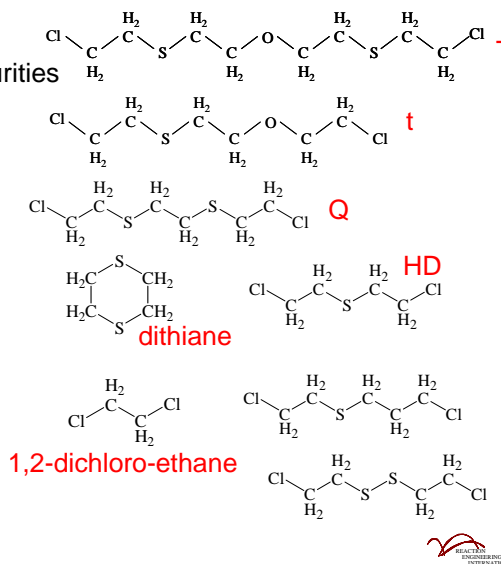
$$\begin{array}{c}
 | \quad | \quad | \quad | \\
 \text{Cl}-\text{C}-\text{C}-\text{S}-\text{C}-\text{C}-\text{Cl} \\
 | \quad | \quad | \quad |
 \end{array}
 \longrightarrow
 \begin{array}{c}
 | \quad | \quad | \quad | \\
 \text{Cl}-\text{C}-\text{C}-\text{S}-\text{C}=\text{C} \\
 | \quad | \quad | \quad |
 \end{array}
 + \text{HCl}$$

$k = 1.85 \times 10^{13} e^{(-58.75/RT)} \text{ sec}^{-1}$

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Thickeners & Impurities

- Kinetics for thickeners and impurities
- H modeled by 6-specie blend
- HT modeled by 5-specie blend

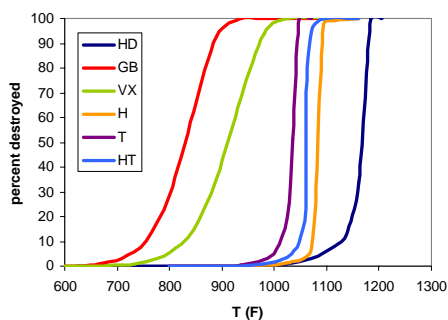


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Calculated Incinerability Rankings

Approximation to UDRI Incinerability Ranking

(Temperature at which 99%
of the compound is
destroyed in 2 seconds)

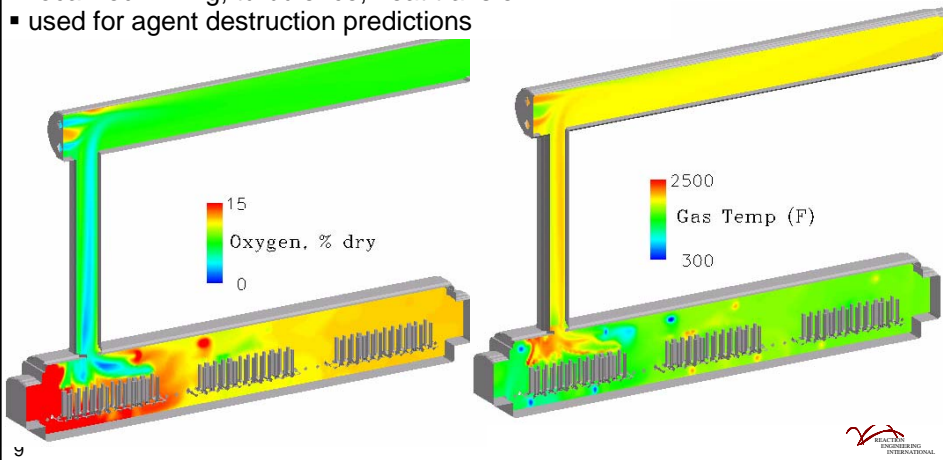


Compound	T99(2)	Class
Benzene	1150 C	1
Toluene	895 C	2
Vinyl Chloride	770 C	3
Trichloroethane	635 C	4
HD	628 C	4
H	603 C	4
HT	578 C	5
T	562 C	5
Chloroform	545 C	5
VX	541 C	5
Hexachloropropene	505 C	5
GB	491 C	5
Strychnine	320 C	6

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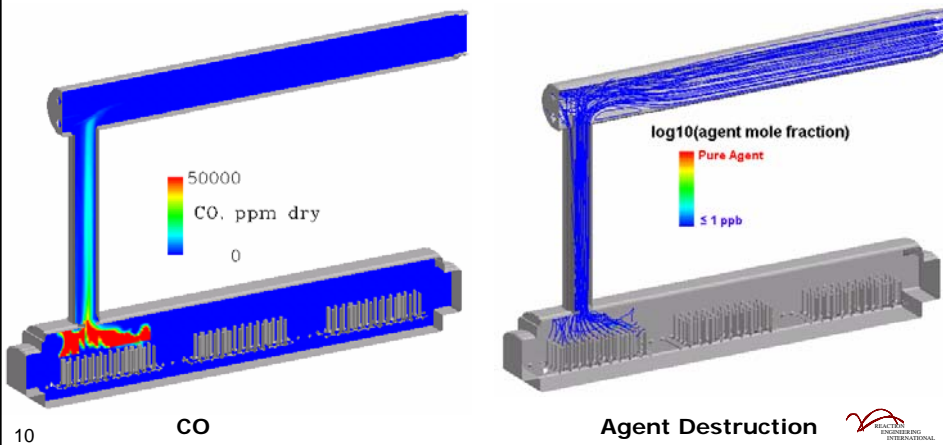
CFD Combustion

- full 3D combustion flow field
 - gas velocity, composition, temperature
 - shell and wall heat transfer, temperature
- localized mixing, turbulence, heat transfer
- used for agent destruction predictions



CFD Model Results & Agent Destruction

CFD Results provide details about agent destruction along streamlines

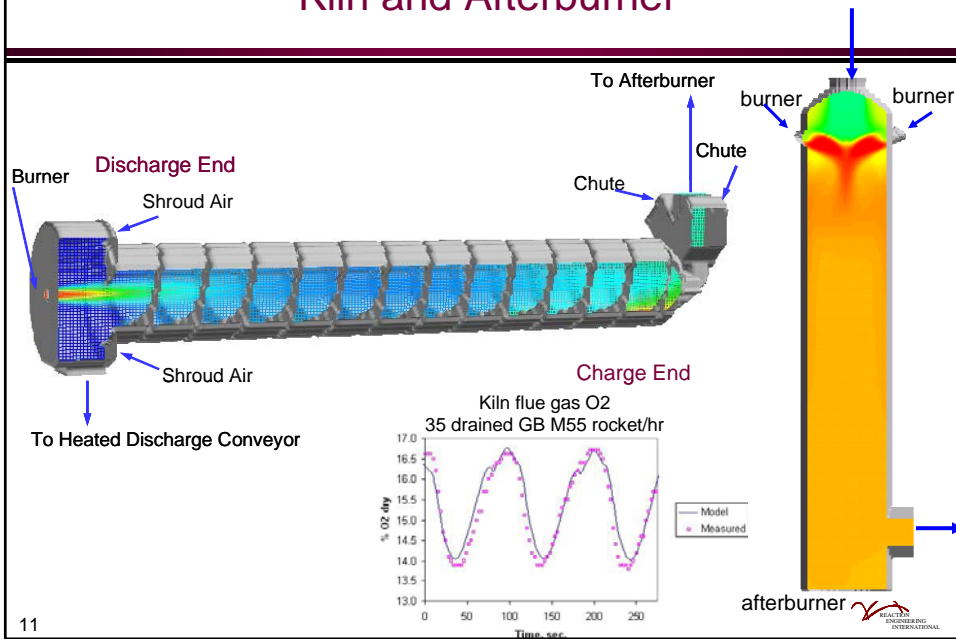


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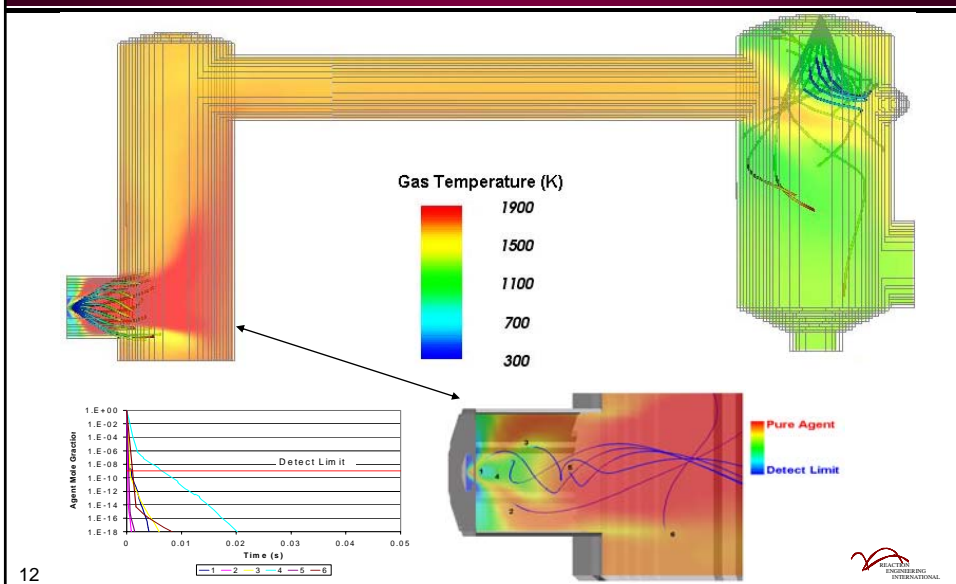
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Agent Destruction

Deactivation Furnace System Kiln and Afterburner



Liquid Incinerator Combustor



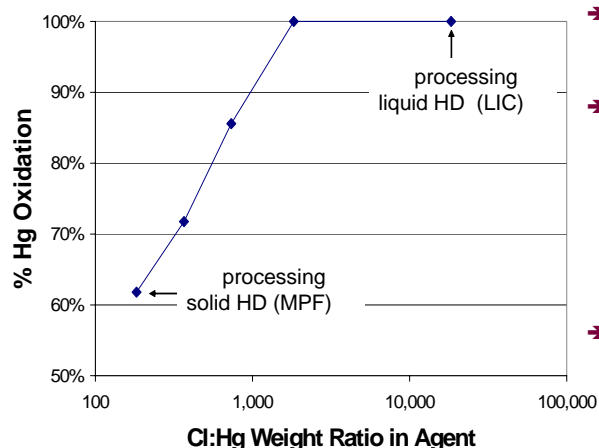
Impact of SBIR Project on Chem Demil Program

- JACADS DAL VX event (RIM 57)
 - ◆ Models used to convince [regulators](#) to modify DAL clearance criterion
 - ◆ Resulted in significant cost savings
- Fate of phosphorus when processing organophosphorus agent
 - ◆ Analysis used in negotiations with [regulators](#)
 - ▶ Obtain "credit" for PFS emissions removal
 - ▶ Replace surrogate trial burn with agent trial burn
 - ▶ Eliminate requirement for high temperature test
- RIM-65 MPF evaluation for processing undrained mustard projectiles (with solid heels)
 - ◆ Analysis to assist TOCDF & ANCDF in negotiations with [regulators](#) to modify incinerator operation
- SBIR Phase II plus
 - ◆ HT mustard chemical kinetic mechanism
 - ◆ Improved understanding of mercury issues
 - ◆ HD TC processing
 - ◆ CMS burner evaluation
- Potentially → extend models to non-incineration *thermal treatment*

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Model Results: Effect of Agent Hg Content on Hg Oxidation



- Shown is calculated Hg oxidation at different ratios of Cl:Hg in feed
- TOCDF HD TCs:
 - ◆ Liquid HD
 - Hg ~ 10's ppm
 - Cl:Hg ~ O(10,000)
 - ◆ Solid agent
 - Hg ~ 100's -1000's ppm
 - Cl:Hg ~ O(100)
- Cl:Hg >2000 results in complete oxidation of Hg in quench tower

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Ramifications of Hg Removal Modeling

- Predicts increased Hg capture when:
 - ◆ increase Cl/Hg ratio in munitions
 - ◆ decrease cooling rate in PAS
- Hg⁰ capture in PAS can be increased by
 - ◆ Increasing Cl/Hg ratio
 - » e.g. add chlorocarbons used in trial burns
 - ◆ Decreasing cooling rate in quench tower
 - » control of quench flow rate or droplet size
- Control of mercury removal in PAS influences waste handling strategies
 - ◆ High Hg removal efficiency
 - waste stream contaminated by Hg⁰ is restricted to brine wastes
 - ◆ Low Hg removal efficiency
 - carbon in the PFS is also contaminated by Hg⁰.

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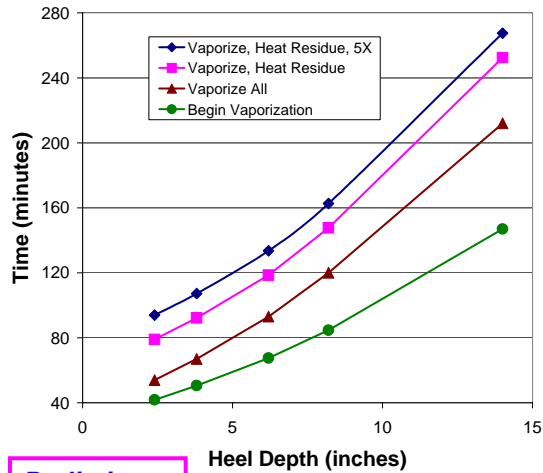
Processing Partially Drained TCs in MPF

- Motivation:
 - ◆ Many mustard ton containers can not be fully drained
 - ◆ What level of solid heel in ton containers can be processed in MPF in a “reasonable time” ?
 - ◆ Use wash-out process or incineration ?

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Feed Cycle (Process) Time Partially Drained Ton Container With Solid Heel



**Preliminary
Results**

- ❖ Peak Vaporization Rate
 - 2.5" heel < 600 lb/hr
 - 14" heel < 1100 lb/hr
- ❖ If all processing in Zone 1 (no overlap) will have long furnace residence time
- ❖ *Opportunity to increase throughput* if overlap zone 1 & 2 processing

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CMS Burner Recommendations From Previous Work



- ➔ Higher temperature alumina-based refractory
- ➔ Lower and/or consistent feed rates
- ➔ Controls improvements
- ➔ Burner modifications

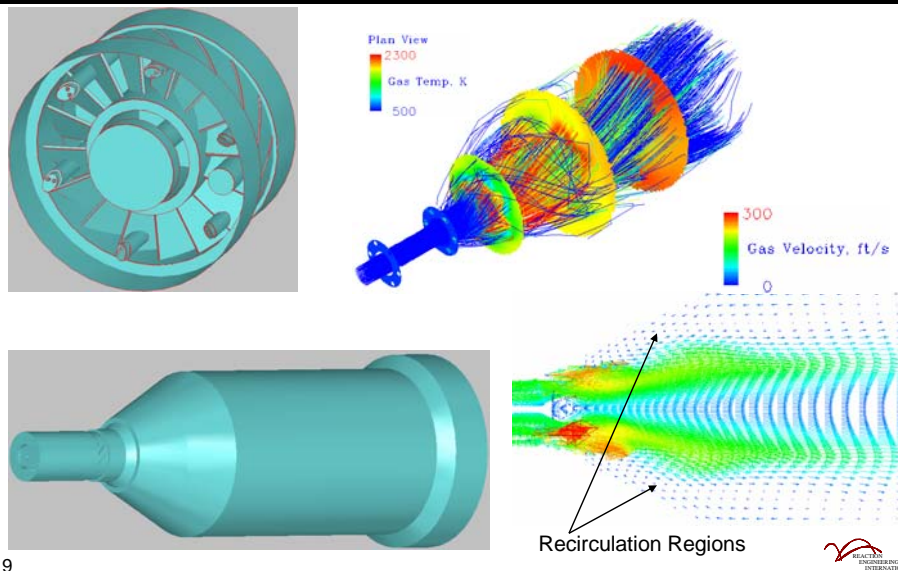
Partial listing of issues raised in one or more of the following studies:

- MicroEnergy Systems, July, 2000
- CR&E, May, 2002
- WDC, May, 2004

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CMS Burner - Deposition Modeling



Value of Project to CMA

- ➔ Demonstrate reliability and performance of existing processes and equipment
- ➔ Assess
 - ◆ trouble shooting / problem solving
 - ◆ proposed design changes
 - ◆ process operation options & optimization
- ➔ Assist Site Operators & Support Contractors

Path Forward

- ➔ Opportunities exist to apply modeling tools throughout the Chem Demil Program
- ➔ Baseline sites (TOCDF, ANCDF, UMCDF, PBCDF)
 - ◆ optimize processing
 - ◆ assistance with troubleshooting
- ➔ Non-baseline sites (where thermal treatment is required)
 - ◆ metal parts, dunnage, carbon

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